

Sodium-Ion Conducting Membranes for Non-Aqueous Redox Flow Batteries

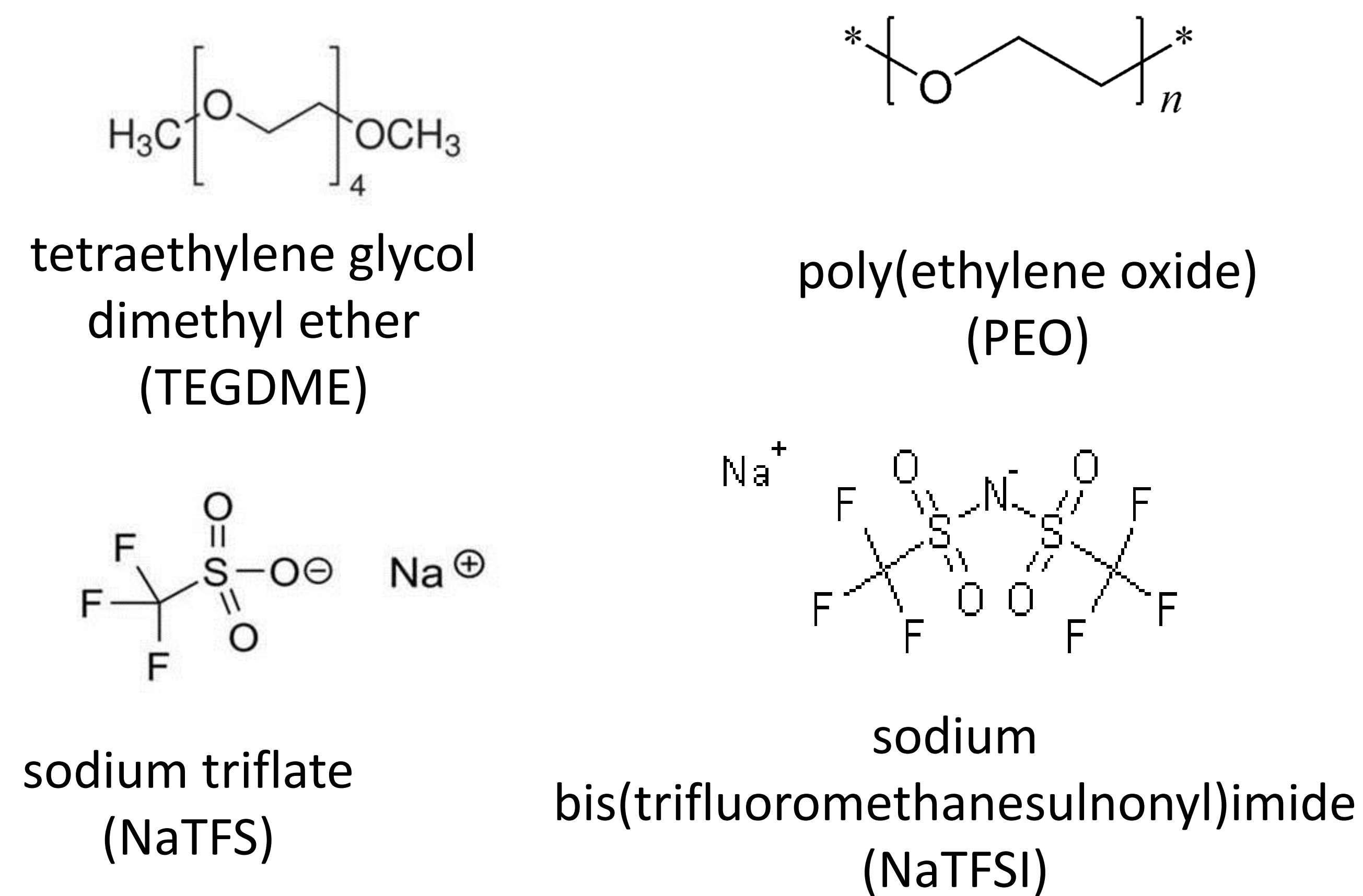
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Abstract

Recently we proposed a new concept for high energy density redox flow batteries that utilize two highly soluble polyaromatic hydrocarbons to mediate reversible redox reactions on the surface of high capacity solid anode materials located in flow reactor reservoirs. Among other things, the success of this technology depends on the development of a membrane separator that has high Na^+ or Li^+ ion conductivity with minimal cross-over. In addition the membrane should be chemically stable with respect to highly reactive anion radicals such as biphenyl $^{\cdot-}$. In an attempt towards achieving such goals, we first improved the ionic conductivity of poly(ethylene oxide) (PEO) membranes by using tetraethylene glycol dimethyl ether (TEGDME) as a plasticizer with sodium triflate (NaTFS) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) as salts. Our results show at least 3 orders of magnitude higher conductivity compared to NaTFS -PEO films. In general films with more plasticizer showed less trans-granular impedance at low temperature, and higher amorphous conduction at higher temperatures. In this study we report Raman and FT-IR spectroscopy to characterize the changes in ion coordination when the salt is dissolved in the plasticizer and PEO blend. Efforts are underway to correlate changes in conductivity with results from Raman and infrared spectroscopy.

Goal: To fabricate a robust and low cost alkali-ion conducting membrane for non-aqueous redox flow battery



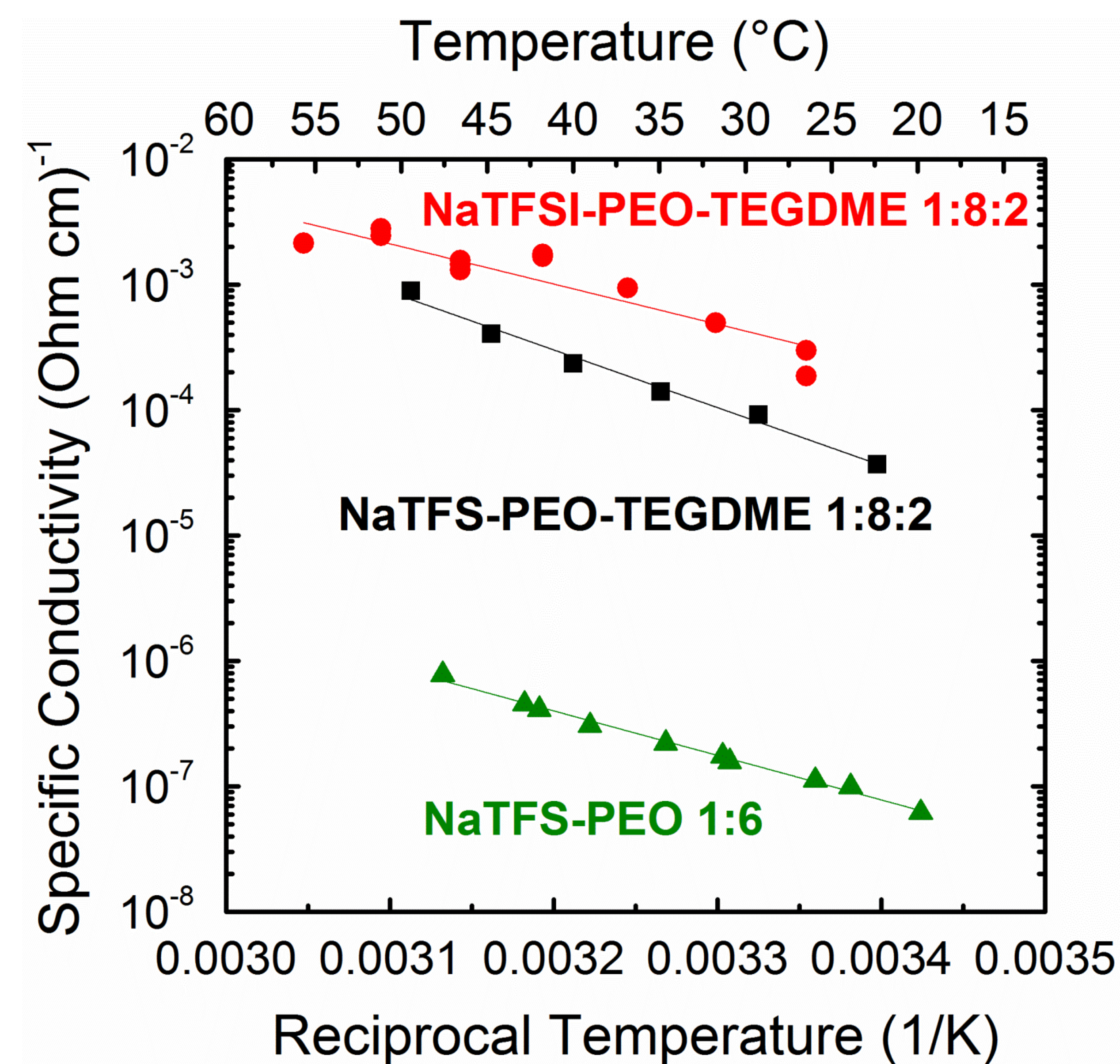
Requirements of a good membrane for radical mediated redox flow battery

- Inert towards anion radicals at strongly reducing potentials
- High ionic conductivity for minimum IR loss and maximum power
- Minimum anion cross-over
- Mechanically stable and robust
- Low cost

Standard membranes like Nafion will not work for this application

Results

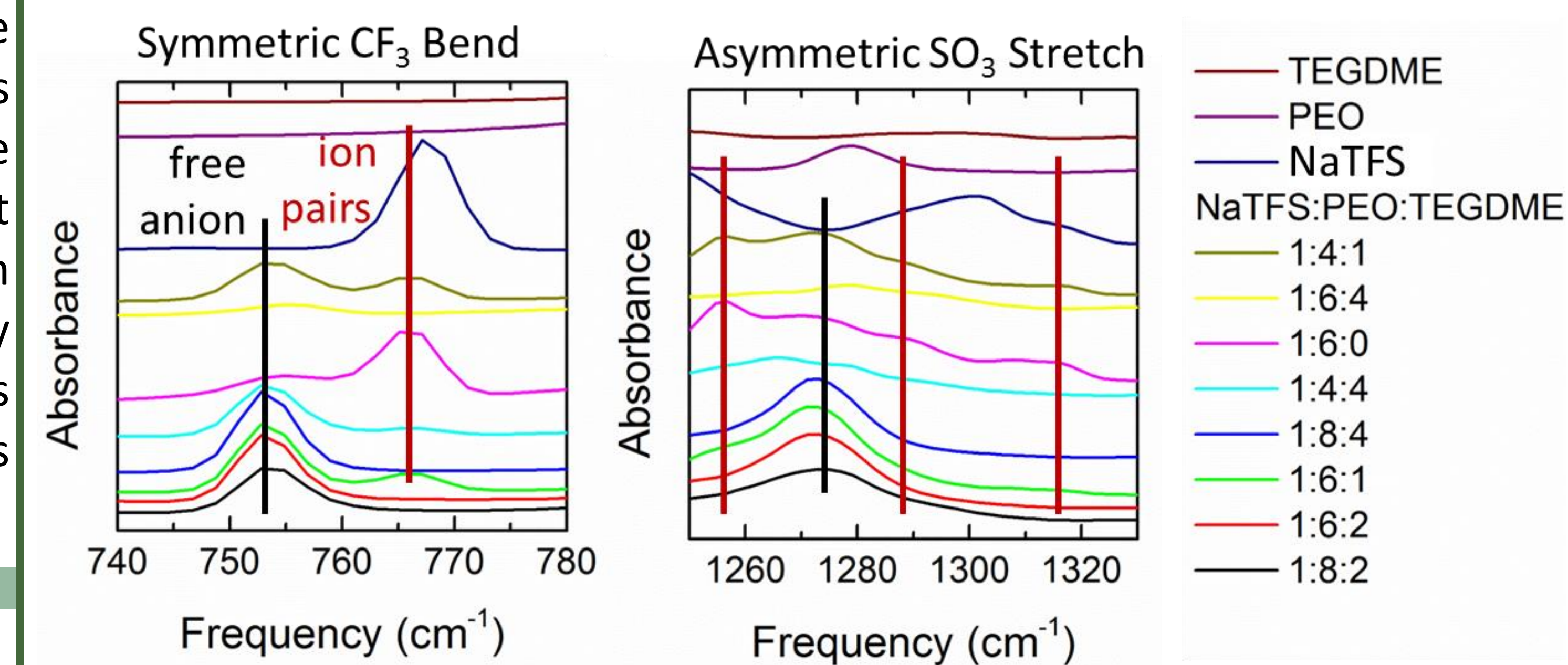
As a plasticizer TEGDME increases ionic conductivity of PEO films by several orders of magnitude



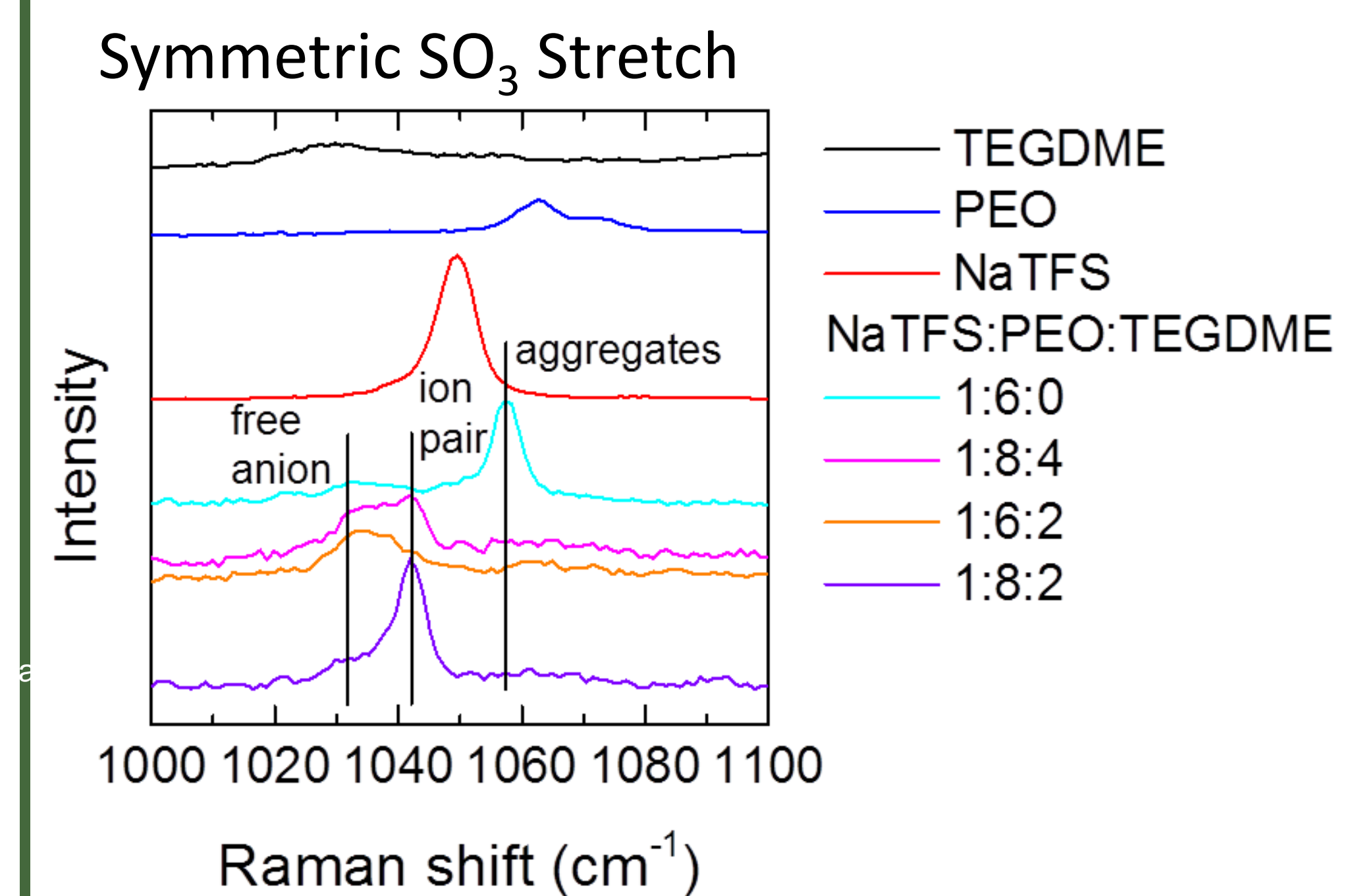
Conductivity vs. inverse temperature of PEO blended with Na salts and TEGDME

- Plasticizing with TEGDME yields 3 orders of magnitude increase in ionic conductivity for NaTFS and 4 orders of magnitude increase for NaTFSI
- Fits Arrhenius behavior with temperature
- This holds true for other compositions with different salt:PEO:TEGDME molar ratios such as 1:4:2, 1:6:2, and 1:8:4
- TEGDME reduces crystallinity and increases free volume
 - less trans-granular impedance at low temperature
 - higher amorphous conduction at higher temperatures

FTIR

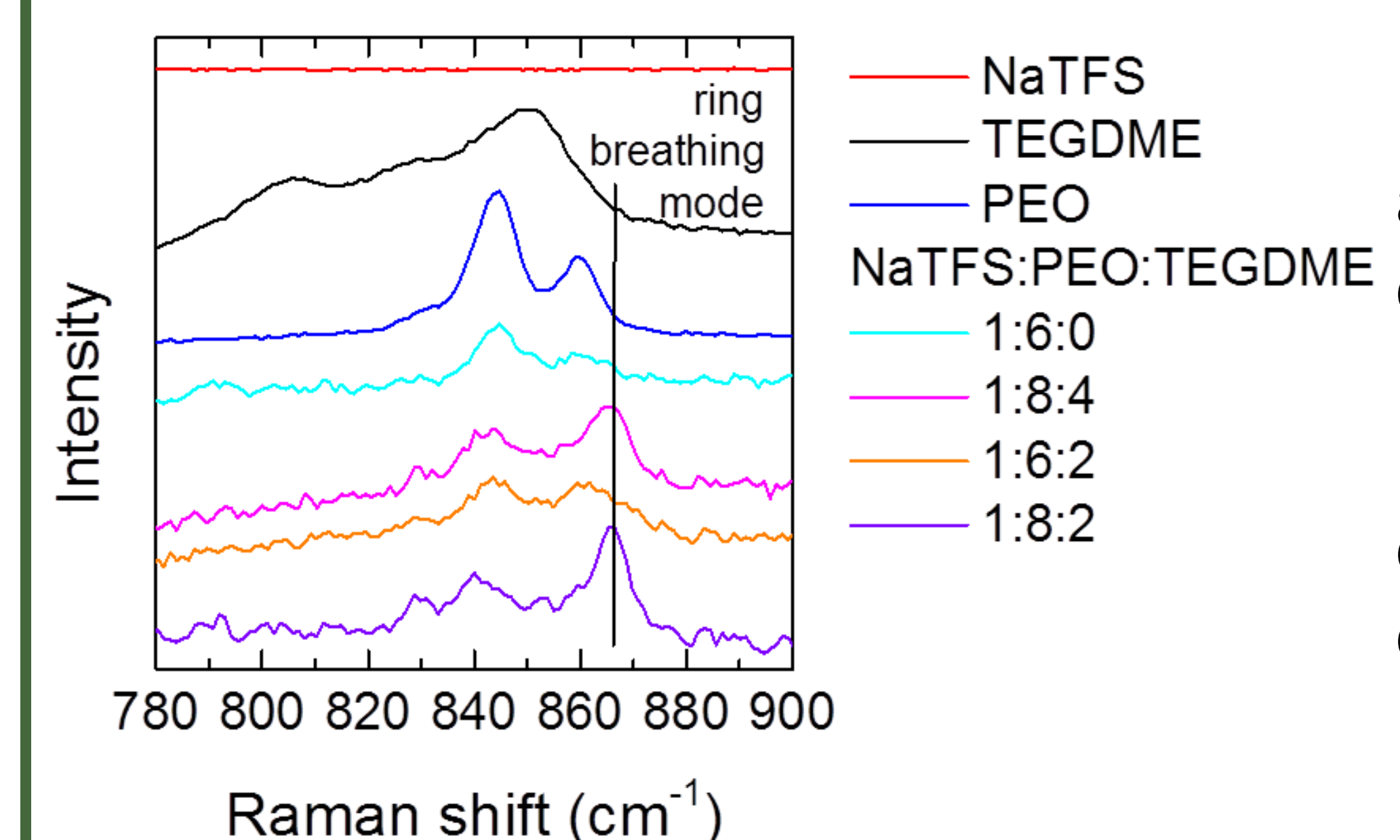


Raman



Shifts in vibrational modes of the triflate anion indicate changes in ion association and coordination environment.

In general, blends with higher TEGDME content have more free anions which correlates with the increase in conductivity.



Band at $\sim 865\text{ cm}^{-1}$ is attributed to a cation-oxygen ring mode of ether molecules coordinating to Na^+ cations.

Future Work

- Improve the mechanical integrity by including structural components to the PEO-TEGDME blend.
- Test membrane resistance and selectivity in anion radical flow cell

Acknowledgements

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